Carrier Density Enhancement in Semiconducting NaSn and CsPb

J. Fortner, Marie-Louise Saboungi, and J. E. Enderby*

Argonne National Laboratory, Argonne, Illinois 60439
(Received 6 September 1994)

The electrical conductivity σ and thermoelectric power S data have been measured in two semiconductors that undergo a solid-state transformation to a dynamically disordered phase about 100 °C below the melting point. At the transition, σ for NaSn is reduced while that for CsPb exhibits a dramatic rise. For both semiconductors, S is reduced in magnitude and changes sign at the transition. These results are consistent with a model which explicitly allows for the interactions between mobile ions and electrons and which provides a unified explanation of the transport properties of these compounds and other fast ion conductors with appreciable electronic conductivity.

PACS numbers: 72.20.Jv, 66.30.Dn

Until recently, the existence of solid rotor phases (i.e., crystals with translational order and orientational disorder) seemed to be confined to inorganic salts with polyatomic ions (e.g., NH_4Cl) or organic molecular crystals (e.g., $C_{10}H_{16}$). Both types of crystals are wide gap insulators so that the electronic conductivity is essentially zero. The situation changed dramatically with the discovery by Price and co-workers [1,2] that the semiconducting compounds CsPb and NaSn, in which charge transfer and directional bonding lead to the formation of Pb_4^{4-} or Sn_4^{4-} Zintl ions, undergo a solid-state first-order phase transition some 100 K below the melting point. The high temperature phases, α-CsPb and α-NaSn, were shown by neutron scattering to be rotor phases. In both cases, the cations (Cs^+ and Na^+) participate in the reorientational motion, the latter undergoing "paddle-wheel" migration, a mechanism first proposed by Lünden [3] to explain the dynamics of Li^+ in α-Li_2SO_4. The object of this Letter is to report the unusual behavior of the electrical conductivity (σ) and thermopower (S) at temperatures above and below the disordering transition (T_c) which demonstrates a direct connection between ionic mobility and carrier concentration.

The compounds were synthesized in the liquid phase from the elements, stated by the suppliers to be of $5N$ quality. All preparative and loading procedures were carried out in an inert glove box, and σ and S were measured on the same sample in an alumina cell using the standard four-probe method [4,5]. Electrical conductivity was measured in the low-temperature (β) and high-temperature (α) solid phases and in the liquid while the thermopower measurements were confined to the solid phases. The data derived from three separate samples and a series of experiments on each sample are shown in Figs. 1 and 2. (For completeness, electrical conductivity for the liquid phases previously measured by van der Lugt and co-workers [6,7] is also displayed and agrees well with our data.) The overall scatter indicates the reproducibility of the results. The qualitative differences between the two compounds is striking. The electrical

conductivities increase with temperature in both β-NaSn and β-CsPb but at the transition show a drop followed by a rapid rise towards the melting point in NaSn, and a jump in CsPb. Note the good agreement between the values of T_c and T_m determined from this work and from an independent thermodynamic study [8,9]. Both systems show a significant decrease in magnitude and a change of sign of S at T_c. The magnitude of S for β-NaSn is remarkably large and remains relatively constant over a wide range of temperature.

We first focus on the β phase of NaSn and both phases of CsPb. In all three phases, σ behaves like that for a conventional semiconductor in the intrinsic temperature regime. If the dominant scattering mechanism of the electrons and holes is due to acoustic phonons, we can express the electron and hole mobilities in the high
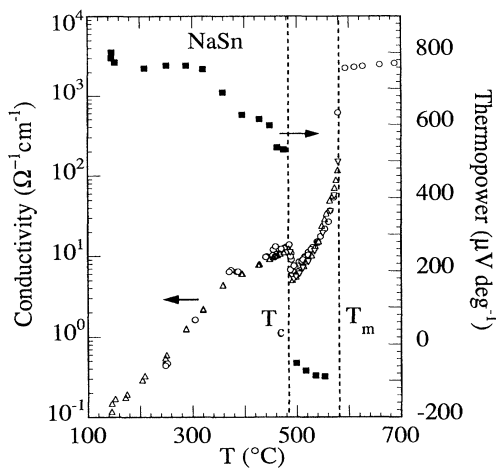

FIG. 1. Electrical conductivity and thermoelectric power data in NaSn. The symbols (open circle and triangles) refer to various sets of electrical conductivity measurements, while the filled squares refer to thermopower measurements [scale on the right hand side (rhs)]. The values of T_c and T_m are taken from an independent thermodynamic study [8].
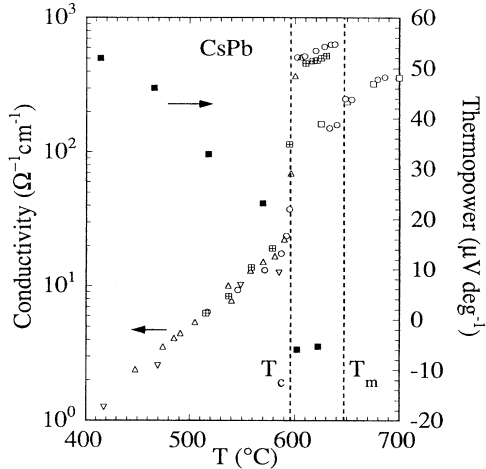
FIG. 2. Electrical conductivity and thermoelectric power data in CsPb. The different symbols refer to various experimental runs for the conductivity, while the filled squares refer to the thermopower (scale on the rhs). The values of T_c and T_m are taken from an independent thermodynamic study [9]. Two sets of data are shown for the liquid (extending into the supercooled region): $\odot$ this study and $\square$ from Ref. [7].

FIG. 3. Electrical conductivity vs $1000/T$ for α-CsPb, β-CsPb, and β-NaSn.

temperature limit as

$$\mu_n = B_n T^{-3/2}, \tag{1}$$

$$\mu_p = B_p T^{-3/2}, \tag{2}$$

so that the intrinsic conductivity σ is given by

$$\sigma = e(n\mu_n + p\mu_p) = eAB\exp[-E_g(0)/2kT], \tag{3}$$

where $B = B_n + B_p$, $A = \frac{1}{4}(2k\sqrt{m_e^* m_h^*}/\pi\hbar^2)^{3/2}\exp(-\beta/2k)$, and the extrapolated energy gap is given by $E_g(0) = E_g(T) + \beta T$. The conductivity in the high-temperature (intrinsic) regime is given by the canonical equation

$$\sigma = \sigma_0 \exp(-\Delta E/kT), \tag{4}$$

where $\sigma_0 eAB\exp(\beta/2k)$ and $\Delta E = E_g/2$. Taking β as 3×10^{-4} eV K^{-1}, a typical value for many semiconductors, and setting $m_e^* = m_h^* = m$ the free electron mass, we are able to estimate the energy gaps and the mobility sum from the $\ln\sigma$ vs $1/T$ plots shown in Fig. 3. The results are presented in Table I. In the case of β-NaSn, the experimentally derived value for the energy gap compares well with the value of $\sim$0.3 eV obtained by Springelkamp et al. [10] using band structure calculations, if one takes into account the errors associated with the numerical determination.

It is straightforward to show, within the same effective mass and acoustic phonon scattering approximations, that the thermoelectric power S is given by

$$S = \frac{k}{e}\left[2 + \frac{E_g}{2kT}\right]r, \tag{5}$$

where $r = (B_n - B_p)/(B_n + B_p)$. Equation (5) implies that the voltage scale for S is 10^3 μV K^{-1}. It follows
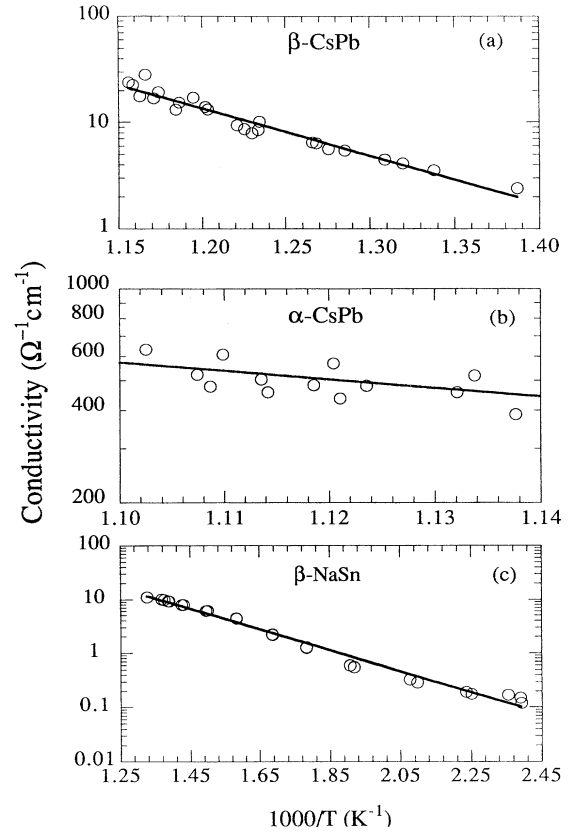
from the data shown in Figs. 1 and 2 that α-NaSn, α-CsPb, and β-CsPb are characterized by r values close to zero, that is to say $B_n \cong B_p \cong B/2$. The data for β-NaSn, on the other hand, require $r \sim -0.9$, implying that $B_p \gg B_n$.

From Table I, β-CsPb is a semiconductor with a large energy gap of 1.69 eV. The magnitude of the conductivity prefactor σ_0 implies that the electron and hole mobilities are very high ($>10^5$ cm^2 V^{-1} s^{-1} at room temperature). In semiconductor physics [11] there is a general tendency for mobility to decrease with increasing energy gap, and thus β-CsPb has considerable potential as a high frequency device and apparently exceeds GaAs (until now regarded as the only semiconductor competitive with Si) in terms of the mobility product $\mu_n\mu_p$ vs E_g (Table II). For nearly all semiconductors, the electron and hole effective masses are less than the free electron value, and, if this situation prevails in CsPb, the actual mobilities are higher than the inferred from the conductivity prefactor. On the other hand, if E_g is assumed to be more strongly dependent on temperature than is usual for semiconductors (i.e., β chosen as 10^{-3} eV^{-1} K^{-1}), then μ_n and μ_p are reduced by a factor of 70. We therefore show the mobility product calculated with several sets of parameters, and it is evident

TABLE I. Experimentally determined values of the transition temperature (T_c), the conductivity prefactors (σ_0), activation energies (ΔE), energy gaps (E_g), and mobilities $(\mu_n$ and $\mu_p)$ in β-CsPb, α-CsPb, and β-NaSn.

Compound	T_c (K)	σ_0 (Ω^{-1} cm^{-1})	ΔE (eV)	$E_g(0)$ (eV)	$\mu_n + \mu_p$ at 300 K (cm^2 V^{-1} s^{-1})	$\mu_n + \mu_p$ at T_c (cm^2 V^{-1} s^{-1})
β-CsPb	873	$(2.8 \pm 0.4) \times 10^6$	0.84 ± 0.01	1.69 ± 0.02	$(1.1 \pm 0.4) \times 10^5$	$(2.4 \pm 0.4) \times 10^4$
α-CsPb	873	$(6.3 \pm 0.5) \times 10^5$	0.52 ± 0.02	1.05 ± 0.04	$[(2.4 \pm 0.5) \times 10^4]$[a]	$(5.3 \pm 0.5) \times 10^3$
β-NaSn	757	$(4.3 \pm 0.5) \times 10^3$	0.37 ± 0.02	0.74 ± 0.04	$(1.8 \pm 0.4) \times 10^2$	48 ± 4

[a]Extrapolated value.

that, even on the most pessimistic assumptions, β-CsPb is competitive with both Si and GaAs. Additional transport measurements (e.g., of Hall coefficients) are clearly necessary if a fuller understanding of the β phase is to be gained. However, the main thrust of this work is to consider the changes in electrical behavior across the transition and we now address this question.

The transition from the ordered to the disordered phase is accompanied by a crystallographic change. NaSn and CsPb are both tetragonal in the β form but above T_c are monoclinic and triclinic, respectively. Thus, the symmetries of the α phases are lower than those of the β phase [12]. (Symmetries of high-temperature phases are normally higher than those of low-temperature phases, although this is not a thermodynamic requirement and exceptions arise when rotational, translational, or other forms of disorder are present.) Moreover, the molar volume of the α-CsPb phase is higher than that of the β phase. It would be expected that the structural changes for NaSn and especially for CsPb would tend to decrease the conductivity by narrowing the energy bands and increasing the energy gap. This is, as we shall see, contrary to the observations.

We therefore consider whether the presence of mobile species can couple directly with the electronic energy states, reflecting a departure from the adiabatic approximation. Such coupling is, of course, at the heart of theories of superconductivity and excitonic insulators, but the possibility of ion-electron interactions modifying the ground state electronic structure of disordered semiconductors has been recently noted by Aschroft [13]. An attempt to estimate the influence of mobile ions on the energy gap in semiconductors was made by Ramasesha [14]. The central assumption in this work is that the mobile ions and electrons have an effective (mean-field) attractive interaction which leads to a lowering of the total free energy. Ramasesha showed that an abrupt transition from an ordered to a dynamically disordered phase is accompanied by a reduction in E_g, the magnitude of which depends, *inter alia*, on the strength of the coupling parameter W; however, he did not take into account the thermodynamic conditions needed for such an abrupt transition. Subsequently, Gurevich and Kharkats [15] derived rigorously an exact formalism which essentially substantiated the earlier conclusions.

If we consider the electrical behavior of CsPb across T_c, we find (Table I) that both the mobility (as derived from σ_0) and E_g are reduced. The reduction in mobility is to be expected on general grounds and reflects the increase in disorder scattering. The reduction in E_g is, we believe, a consequence of the interaction between mobile ions and the electron states, as first suggested by Ramasesha.

We next consider the high-temperature form of NaSn. Unfortunately, and unlike the other phases considered in this Letter, the conductivity data are not readily interpreted

TABLE II. Compiled values of the energy gap (E_g), the mobility product $(\mu_n\mu_p)$, and ratios of effective masses (m^*) and the temperature coefficient of the energy gap β for selected semiconductors.

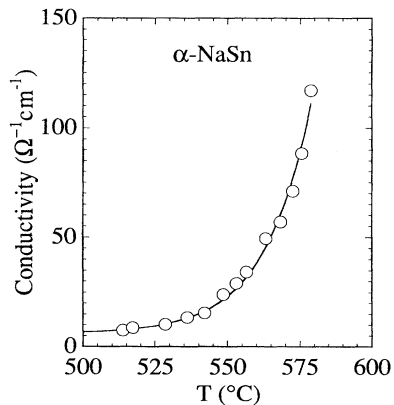| Compound	$E_g(0)$ (eV)	$\mu_n \mu_p$ at 300 K (cm^4 V^{-2} s^{-2})	m_e^*/m	m_h^*/m	β (eV K^{-1})
Si[a]	1.153	5.32×10^5	0.44	037	2.4×10^{-4}
GaAs[a]	1.47	1.44×10^6	0.06	0.44	4.4×10^{-4}
β-CsPb	1.69		1	1	
		2.96×10^9	0.4	0.4	3×10^{-4}
		4.73×10^{10}	$\cdot 1$	1	3×10^{-4}
		6.41×10^5	0.4	0.4	10^{-3}
		1.02×10^7			10^{-3}

[a]See Ref. [11].

FIG. 4. Electrical conductivity of α-NaSn. The open circles represent data and the solid line the empirical fit $\sigma(\Omega^{-1}\,cm^{-1}) = (4.65 + 1.07) \times 10^{-19}\exp\{0.057T(K)\}$.

in conventional semiconductor terms. Immediately above T_c, $\sigma \sim 5\,\Omega^{-1}\,cm^{-1}$, a value consistent with reductions in σ_0 and E_g, is comparable with those for CsPb. In the α phase, E_g closes rapidly with temperature (i.e., as T^n with $n > 1$), so that metallic values of σ are achieved as the melting point is approached (Fig. 1). It was shown [14,15] that, for certain values of the coupling parameter, E_g continues to collapse in the mobile phase with increasing temperature, and this effect appears to dominate the behavior of α-NaSn. In fact, the observed conductivity can be empirically expressed by the formula $\sigma(\Omega^{-1}\,cm^{-1}) = 4.65 + 1.07 \times 10^{-19}\exp\{0.057T(K)\}$, the second term of which reflects the rapid disappearance of the energy gap as T increases (Fig. 4). However, since the dependence of the concentration of mobile electrons and ions on temperature in these mixed conductors cannot be assessed from the present data, only a cooperative disordering can be advanced.

We finally note that Xu, de Groot, and van der Lugt [16] have measured the electrical conductivity of the high-temperature phase of Mg_3Bi_2. The temperature dependence of σ closely resembles that of NaSn, in particular $\sigma \propto T^n$ with $n > 1$, although the absolute value is 2 orders of magnitude greater. No explanation for this unusual behavior has yet been offered. Recently, however, Barnes, Guo, and Howells [17] have shown that the high temperature phase of Mg_3Bi_2 is in fact a fast ion conductor, the mobile species being Mg^{2+} cations. These two observations, hitherto unrelated, are presented as further evidence that ionic motion does indeed couple strongly with the electrons. Similar considerations should apply to the changes in electronic properties across the superionic ($\beta \rightarrow \alpha$) transition of Ag_2Se and Ag_2S, which have long been regarded as something of a puzzle [18]. The energy gaps of both compounds disappear at the transition, notwithstanding a significant volume expansion. In summary, at a dynamically disordering

(superionic or rotor) transition in a semiconductor, many certainly influence σ and S. Nevertheless, the fact that a wide variety of systems conform to a single pattern of behavior strongly suggests that the changes in σ and S at the transition have a common origin—the creation of mobile ions which influences the electron state in a manner which transcends the adiabatic approximation.

*Permanent address: University of Bristol, Department of Physics, Bristol, England.

[1] D. L. Price, M.-L. Saboungi, H. T. J. Reijers, D. Kearley, and R. White, Phys. Rev. Lett. **66**, 1894 (1991).

[2] M.-L. Saboungi, J. Fortner, W. S. Howells, and D. L. Price, Nature (London) **365**, 237 (1993).

[3] A. Lünden, Solid State Ionics **68**, 77 (1994), and references therein.

[4] A. C. Barnes, Ph.D. thesis, University of Bristol, 1985.

[5] J. Fortner, M.-L. Saboungi, and J. E. Enderby, Philos. Mag. Lett. **68**, 85 (1993).

[6] C. van der Marel, A. B. van Oosten, W. Geertsma, and W. van der Lugt, J. Phys. F. **12**, 2349 (1982).

[7] J. A. Meijer, G. J. B. Vinke, and W. van der Lugt, J. Phys. F. **16**, 845 (1986).

[8] M.-L. Saboungi, G. K. Johnson, and D. L. Price, in *Statics and Dynamics of Alloy Phase Transformations*, edited by P. E. A. Turchi and A. Gonis (Plenum Press, New York, 1994).

[9] M.-L. Saboungi, H. T. J. Reijers, M. Blander, and G. K. Johnson, J. Chem. Phys. **89**, 5869 (1988).

[10] E. Springelkamp, R. H. de Groot, W. Geertsma, W. van der Lugt, and F. M. Mueller, Phys. Rev. B **32**, 2319 (1985).

[11] H. F. Wolf, *Silicon Semiconductor Data 1969* (Pergamon Press, Oxford, 1969).

[12] D. L. Price, M.-L. Saboungi, and J. W. Richardson (unpublished).

[13] N. W. Ashcroft, J. Non-Cryst. Solids **156–158**, 621 (1993).

[14] S. Ramasesha, J. Solid State Chem. **41**, 333 (1982).

[15] Y. Y. Gurevich and Y. I. Kharkats, Fiz. Tverdogo Tela (Leningrad) **27**, 1977 (1985) [Sov. Phys. Solid State **27**, 1188 (1985)].

[16] R. Xu, R. A. de Groot, and W. van der Lugt, J. Phys. Condens. Matter **5**, 7551 (1993).

[17] A. C. Barnes, C. Guo, and W. S. Howells, J. Phys. Condens. Matter **6**, 2467 (1994).

[18] P. Junod, H. Hediger, B. Kilchör, and Wullschleger, Philos. Mag. **36**, 941 (1977).